

Controlling structure in associating polymer–surfactant mixtures*

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Abstract: Structures of concentrated mixtures of associating polymer–surfactant mixtures are important in many technical applications. Yet an in-depth understanding of how molecular parameters affect these structures is lacking. We here summarize the results of ongoing work using a novel simplified approach to the study of associating oppositely charged polymer–surfactant mixtures, introducing a minimum number of components to the various mixtures. The results illustrate the relations between systems with and without polyions, as well as effects of systematic changes of parameters such as surfactant chain length, polyion length, polyion charge density, and the charge density of the surfactant aggregate.

Keywords: polyelectrolytes; surfactants; phase behavior; structures; liquid crystals.

INTRODUCTION

A most fascinating and useful aspect of surfactant molecules is their ability to self-assemble in an aqueous environment into aggregates of different geometries which, in turn, can organize into a multitude of structures. A particularly rich example is the nine different structures found in the phases of one single block copolymer/water/oil system, illustrated in Fig. 1 [1]. The properties of the various surfactant phases differ very much, depending on their structure. Some are anisotropic, others isotropic. Some aggregates are finite, whereas others are continuous in one, two, or three dimensions, with obvious consequences for the diffusion of molecules confined in the separated hydrophobic or hydrophilic domains. Some aggregates pack in a disordered fashion, whereas others organize into structures that display long-range liquid-crystalline order. The presence or absence of long-range order greatly affects the rheology of the system. For instance, the macroscopic appearance of a micellar cubic phase is that of a hard solid, whereas a disordered micellar solution—at the same surfactant concentration—may be a viscous, but readily pourable, liquid.

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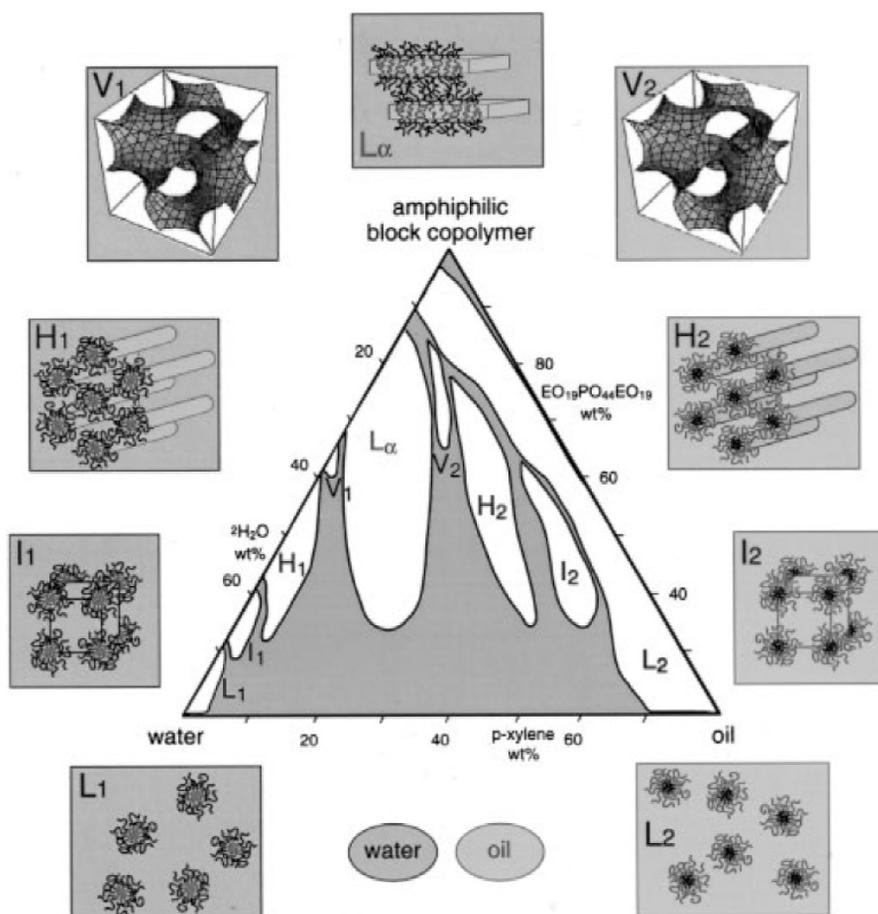


Fig. 1 Amphiphilic molecules can form a multitude of structures. Phases formed by the triblock copolymer $\text{EO}_{19}\text{PO}_{44}\text{EO}_{19}$, based on ethylene oxide and propylene oxide monomers, mixed with water and *p*-xylene. L = disordered micellar, I = micellar cubic, H = hexagonal, V = bicontinuous cubic, and L = lamellar. From ref. [1].

Polymers are mixed in surfactant systems for a number of reasons. In disordered surfactant solutions, the objective might be to simply increase the viscosity. However, often the interactions between polymer and surfactant molecules are used to control the phase behavior of the mixture. As is well understood, mixed polymer–surfactant solutions have a strong tendency to phase-separate, compared to similarly concentrated mixtures of small molecules. This is because the translational contribution to the entropy of mixing is small in mixtures of large molecules or aggregates, where the number of particles is small. Thus, two classes of phase separation are commonly encountered in polymer–surfactant mixtures (Fig. 2): *segregation*, where the polymer and surfactant components are enriched in separate phases, and *association*, where the two components are enriched in the same phase [2,3]. This tendency for phase separation of polymer–surfactant mixtures may be utilized in various ways. Segregating systems may be used, for instance, in aqueous separation systems [4]. Both segregating and associating mixtures can be used to concentrate surfactant systems; however, the associating mixtures generally require less material, since the surfactant-poor phase in this case is typically a dilute aqueous solution. A common usage of associating mixtures is in formulations where one wishes to deposit material as an insoluble layer on a surface.

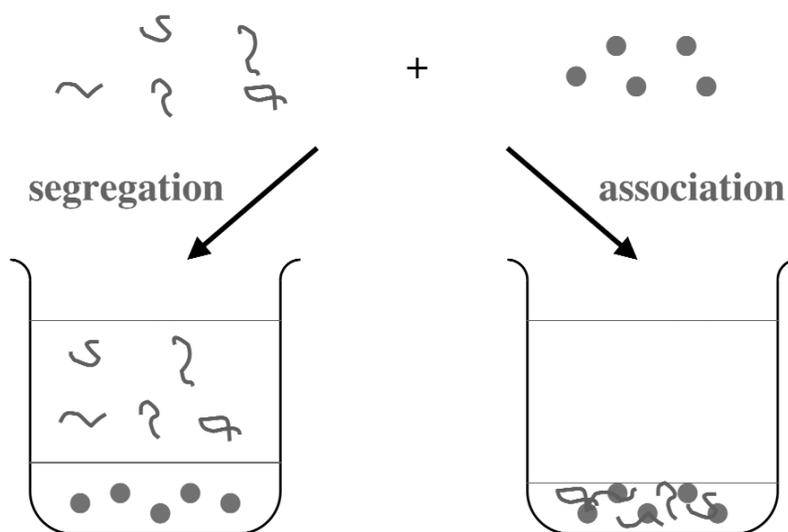


Fig. 2 Mixtures of polymer molecules and surfactant aggregates in a common solvent typically phase-separate.

Another context where polymer–surfactant mixtures are widely used is generally known as “surfactant templating”. Progress in this very active area is described in several recent reviews [5–10]. The idea here is to use the organized surfactant structure as a “template” or a “structure guiding agent” in a polymerization reaction, the result of which is a structured, mesomorphous material. If the polymerization is performed in the aqueous domain, the polymerized material will be a replica of the structure formed by the surfactant aggregates. Very often, such reactions are performed using silicate monomers, and the resulting material then becomes a structured, mesoporous silica. It is essential in these applications to realize that a consequence of any polymerization process is to decrease the translational entropy of mixing in the system, as was pointed out above. Thus, a polymerization will often result in a phase separation. If a repulsive monomer–surfactant couple is used in the polymerization, the polymerized component may separate out from the surfactant-rich phase—a mostly undesired result. Clearly, a successful incorporation of polymer and surfactant in the same structure is most readily achieved if one uses an associating polymer–surfactant pair. This is indeed the case in formulations used in practice.

Thus, associating polymer–surfactant systems are found in many contexts. In all of these, it is important to be able to control the composition and the resulting structure of the associating polymer–surfactant phase under the conditions when it forms, which is typically as a concentrated phase that separates out from a dilute phase containing mostly water. For conventional simple surfactants in water, we have a very good understanding, based on a wealth of experimental and theoretical work, on how to tune the structure and composition of the system by adjusting the chemical structure of the surfactant and/or by adding oil or salt. A similar good understanding is not available for surfactant phases that also contain polymers. Two central, but largely unanswered, questions are as follows.

1. How can we understand the structures obtained in associating polymer–surfactant mixtures, particularly in terms of the molecular features of the polymer?
2. How are polymer-containing surfactant phases related to conventional surfactant phases?

There are different classes of associating polymer–surfactant couples, but most common are those where the association is driven by charges of opposite sign on the polymer–surfactant molecules. During the last decade, a number of laboratories have studied the structures of the concentrated phases separating out from oppositely charged polymer–surfactant mixtures [11–20]. Generally, the same types of structures are found in these phases as in concentrated solutions of the ionic surfactants alone, that

is, disordered micellar, cubic, hexagonal, or lamellar. This is also true for the structures that are formed when inorganic monomers, such as silicates, are polymerized in dilute solutions of cationic surfactants [6,7,10].

Naturally, conventional studies of oppositely charged polymer–surfactant systems involve mixtures of a *polyelectrolyte* (polyion + simple counterion) with an ionic *surfactant* (surfactant ion + simple counterion) in water. A problem with such mixtures, however, is that the phases separating out from them generally cannot be described as mixtures of polyelectrolyte, surfactant, and water, since typically one phase will be enriched in both the polyion and the surfactant ion, while the simple ions distribute more uniformly. In general, each phase will contain all four ions in proportions that cannot be predicted a priori, but have to be measured. Indeed, even such a simple process as dilution by water may dramatically change the proportions of the ions in the coexisting phases [15]. A phase-separated mixture is thus a four-component system, where the composition of each phase can be described as a combination of three different neutral salts and water. This situation is illustrated in Fig. 3, with the help of the pyramid phase diagram introduced by Thalberg [21]. This diagram features water in the apex and the four possible binary neutral salts in the corners of its quadratic base. Figure 3 illustrates that a phase separation occurring in a mixture prepared in the conventional mixing plane of polyelectrolyte and surfactant typically results in one concentrated phase, enriched in the *complex salt* (surfactant + polyion) and one dilute phase, containing mostly the *simple salt* (simple cation + simple anion). For the molecular interpretation, and theoretical modeling, of such properties as size, shape, and packing of the surfactant aggregates, a knowledge of the composition of the system is essential. It is also highly desirable to be able to vary the composition within a concentrated phase in a systematic way, without being limited to the particular compositions that result from the phase separation of mixtures of polyelectrolyte and surfactant.

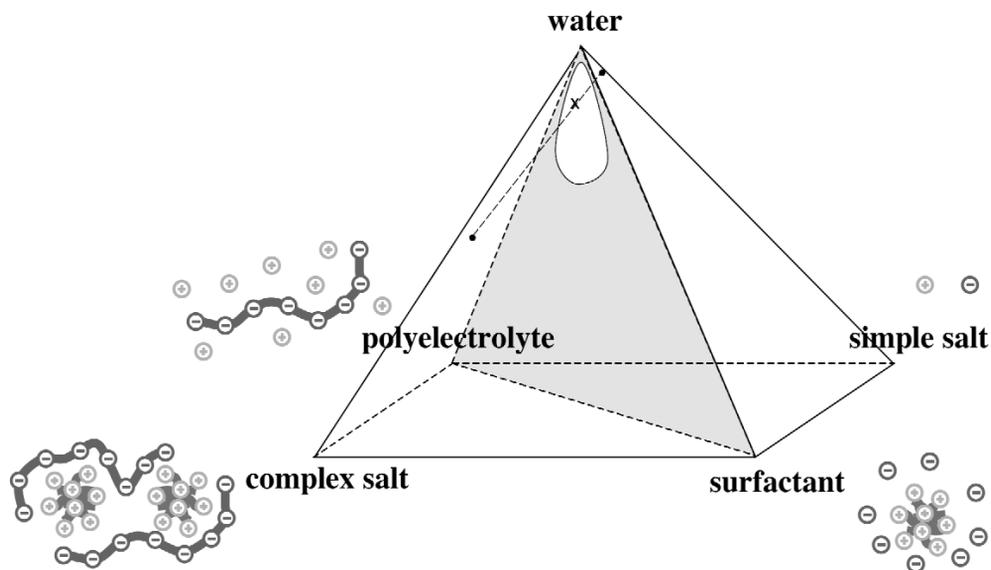


Fig. 3 Pyramid representation [21] of the phase diagram of mixtures of a polyelectrolyte and an oppositely charged surfactant, featuring the four possible combinations of the four ions into binary neutral salts. The conventional mixing plane (shaded) and a typical result of a phase separation (tie-line) are indicated in the diagram.

In an ongoing systematic work at our laboratories [22–27], aimed at a molecular understanding of the structures and water uptake of oppositely charged polymer–surfactant systems, we are using a simplified approach that was recently introduced by one of our laboratories [22]. The idea, illustrated

in Fig. 4, is to synthesize the pure complex salt, containing no simple ions, and to use this salt as the point of departure. The complex salt can be mixed with water, to study the simple dilution process, and then any third component can be added, to study the effect of excess surfactant, excess polyelectrolyte, added oil, and so forth. Each study is thus performed on a maximally simple system containing a minimum number of components. The purpose of the present review is to demonstrate the power of this approach, and to summarize the molecular understanding that has emerged so far.

Study basic mixture: complex salt in water



Make any of the following additions

surfactant salt



uncharged polyacid



polyelectrolyte



cosurfactant



Fig. 4 Simplified strategy for studying oppositely charged polymer–surfactant mixtures using the minimum number of components.

EXPERIMENTAL PROCEDURES

Detailed information on materials and methods are given in the original publications [22–27]. Here, we give a brief summary for the convenience of the reader.

Complex salts

In the studies summarized here, the complex salts were based on polyacrylate (PA_m) and cationic alkyltrimethylammonium (C_nTA^+) surfactants. Here, the indices m and n designate the weight average number of repeating units in the polyion chain, and the number of carbons in the surfactant chain, respectively. The complex salt was produced in a simple acid–base titration, where the cationic surfactant was first ion-exchanged to the hydroxide form, which was then titrated to the equivalence point with the acid form of the polymer, polyacrylic acid (PAA). The complex was then freeze-dried.

Other methods to produce complex salts from conventional polyelectrolyte–surfactant salt mixtures have been used in other work, such as extraction of the complex salt in organic solvents [28] and dilution of a one-phase solution containing excess surfactant, followed by copious washing to remove excess surfactant ions and simple ions [24].

Methods

Sample preparation

Samples were produced by vortex mixing of the dry components and water in the desired proportions in glass tubes, which were then flame-sealed. The samples were further mixed by repeated centrifugation of the tubes, which were turned end over end between centrifugations. The samples were then left to equilibrate for at least several weeks.

Analysis of phases

Samples equilibrated as described above were inspected visually between crossed polarizers to check for anisotropy. Selected samples were analyzed further by small-angle X-ray scattering (SAXS).

MOVING ON THE SURFACE OF THE PYRAMID

Two ternary phase diagrams

By studying ternary mixtures of polyelectrolyte, complex salt, and water on the one hand, and complex salt, surfactant, and water on the other hand, it is possible to make a series of ternary mixtures with compositions that vary continuously from pure polyelectrolyte solutions to pure surfactant solutions. This series will occupy two surfaces on the pyramid phase diagram. This is illustrated in Fig. 5 for a very simple set of components where the polyelectrolyte is NaPA₃₀, the complex salt is C₁₆TAPA₃₀, and the surfactant is C₁₆TAAc [23]. The acetate ion with its carboxylate groups is chemically similar to the polyion, and the short polyion contains fewer charges than the spherical C16 surfactant micelle, where the aggregation number is around 100. A number of conclusions of fundamental nature may be drawn directly from these phase diagrams.

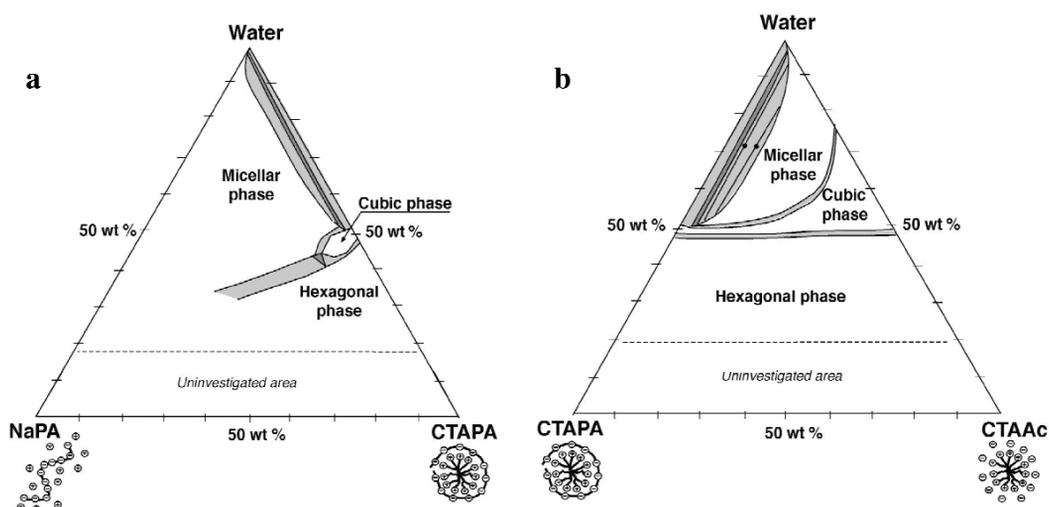


Fig. 5 Ternary phase diagrams for the systems NaPA₃₀/C₁₆TAPA₃₀/water (a) and C₁₆TAPA₃₀/C₁₆TAAc/water (b). The two diagrams correspond to two surfaces of the pyramid diagram in Fig. 3. Together, they represent a continuous series of three-component mixtures extending from the binary polyelectrolyte/water system, via the binary complex salt/water system, to the binary surfactant/water system. From ref. [23].

Complex salt structures are directly related to conventional surfactant structures

The diagram in Fig. 5b features two liquid-crystalline phases, one micellar cubic phase of the Pm3n type and one hexagonal phase. The phase diagram shows that both phases are continuous all the way from the binary complex salt/water axis to the binary surfactant/water axis. The identity of the structures was confirmed by SAXS measurements.

The pure complex salt is a state of minimal mutual solubility with water

The maximum uptake of water by the C_{16} TAPA₃₀ salt in equilibrium with excess water is ca. 50 wt %. At this point, the aqueous complex salt forms a micellar cubic phase with a surfactant aggregation number of ca. 100 [23,25]. The solubility of the complex salt in water is extremely low [25]. When either excess polyelectrolyte or excess surfactant is added to the binary complex salt/water mixture, the miscibility increases very rapidly. This is a consequence of the entropy of mixing of the simple counterions (sodium or acetate, respectively), which rapidly become numerous as the content of polyelectrolyte or surfactant is increased.

A model colloid system

The mixtures shown in Fig. 5 are well suited for theoretical modeling of the phase stability of mixtures of charged colloids with oppositely charged polyions, since they contain the minimum number of components (no added salt). In particular, the C_{16} TAPA₃₀/ C_{16} TAAc/water system (Fig. 5b) at water content above ca. 50 wt % represents a simple system where the micelles are close to spherical, with a constant aggregation number, in both the disordered micellar and the cubic phases. Here, one can see the result of gradually replacing monomeric surfactant counterions with short polymeric counterions. The first notable effect is a rapid shrinking of the cubic phase toward lower water content. With only monomeric counterions present, the repulsion that gives rise to the packing into a cubic structure emanates from the diffuse double layer, rather than the bare particle size of the surfactant aggregate. When some polymeric counterions are present, these will introduce local attractions between pairs of micelles, leaving most of the micelles unaffected. This heterogeneity in the micelle–micelle interactions will tend to destroy the long-range order. At intermediate contents of polymeric counterions, a large disordered micellar phase develops with, eventually, a coexistence between a concentrated and a dilute branch. Finally, at high contents of polymeric counterions, the system is a concentrated cubic phase in equilibrium with almost pure water, as described above. In summary, when simple counterions are replaced by polymeric counterions, the effective interaction between the micelles changes from repulsive to attractive. This effect is fundamentally entropic in origin, since the only parameter that changes is whether or not the counterions are separate or connected in chains. The sequence of phases is quite analogous to that observed in the density–temperature phase diagram of a simple one-component fluid, which features gas–liquid, liquid–solid, and gas–solid equilibria [29]. In the latter system, temperature is used to moderate the entropy contribution to the total Gibbs energy of mixing.

The simple counterion may be important

The acetate ion is an uncommon counterion in cationic surfactants. Figure 6 shows a phase diagram for the same complex salt as in Fig. 5b, but now in mixtures with the common C_{16} TABr surfactant [22]. The change of simple surfactant counterion has dramatic consequences for the phase behavior; the cubic phase disappears almost completely, and the maximum water uptake of the concentrated surfactant phases decreases over most of the mixing range. This may be attributed to the fact that the bromide ion induces a decreased curvature and, hence, a growth of the surfactant aggregate [22,30,31]. Evidently, fewer polyions (per surfactant ion) are required to separate out long rod-like surfactant aggregates compared to small spherical aggregates.

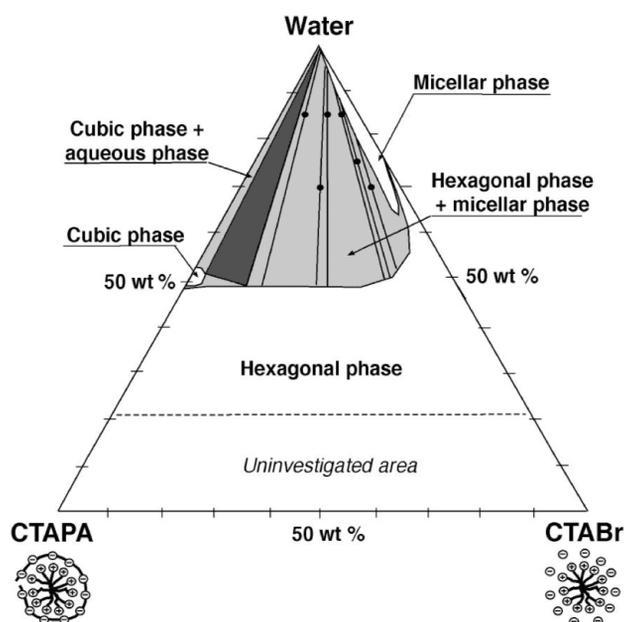


Fig. 6 Ternary phase diagram for the system $C_{16}TAPA_3/C_{16}TABr$ /water. From ref. [22].

INSIGHTS INTO PROCESSES

Before we continue to discuss other mixtures, we note that in principle, a phase diagram provides predictions of the outcome of common processes, where the compositions of the systems change with time. Although it should be borne in mind that, during the course of such a process, the structure may not reach equilibrium, knowledge of the equilibrium state of the system at each point during the process should still provide useful insights.

Drying/dilution

Removal or addition of water is very common in applications. In Fig. 7a, two scenarios resulting from drying or dilution processes are indicated by arrows pointing away from or toward the water corner in the phase diagram. The beginning and the end of an arrow represent the initial and the final states, respectively. The two arrows shown provide the following important predictions regarding oppositely charged polymer–surfactant mixtures.

1. Even if the concentrated phase that separates out from a biphasic mixture has a disordered micellar structure, it may undergo a series of transitions to a sequence of liquid-crystalline phases on drying.
2. A disordered micellar solution may phase-separate on dilution into a concentrated liquid-crystalline phase in equilibrium with almost pure water.

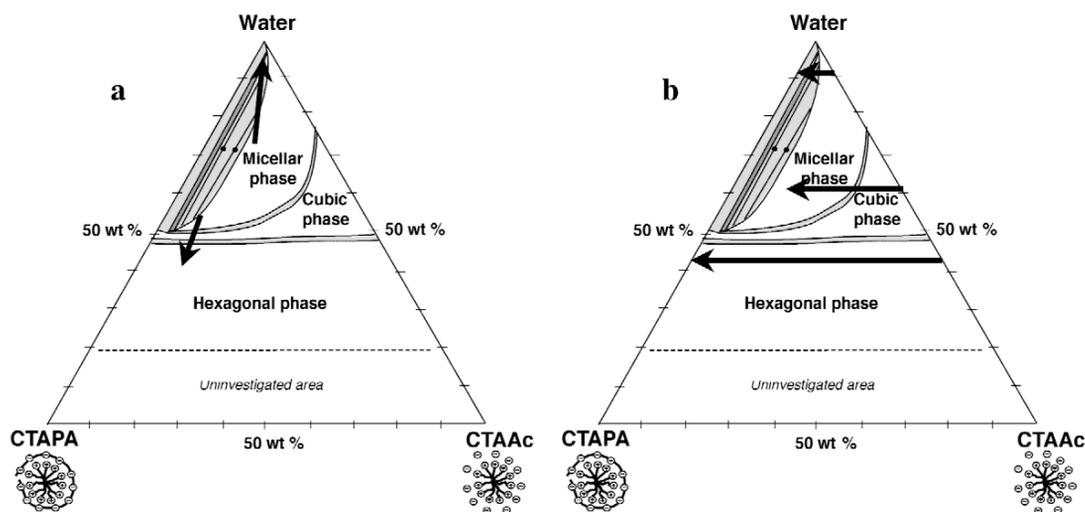


Fig. 7 Phase diagrams provide predictions of the outcome of various processes, such as changing the water content (a) or polymerizing the surfactant counterion (b); see text.

Polymerization

Figure 7b shows pathways, represented by horizontal arrows in the phase diagram, where monovalent counterions are fully or partially replaced by polymeric counterions. Such pathways essentially represent polymerization processes. For the particular phase diagram shown, the arrows drawn predict the following results, some of which are rather nontrivial, of polymerization processes.

1. It is possible to polymerize the counterions of a hexagonal phase without changing the structure.
2. A partial polymerization of the counterions in a cubic phase may result in a change of the system to a viscous disordered micellar solution.
3. Polymerization of the counterions in a dilute micellar solution may result in the formation of a concentrated, ordered cubic phase, containing polyions and surfactant aggregates, in equilibrium with essentially pure water.

The last scenario is indeed a process that is used routinely in the synthesis of mesoporous inorganic materials by polymerizing silicates in dilute solutions of cationic surfactants [10]. As will be illustrated below, small differences in the polymerization process, such as an increase in the molecular weight of the polyion, could produce a hexagonal structure instead.

MODIFYING MOLECULES AND AGGREGATES

Polymer–surfactant mixtures offer many possibilities to tune the properties of the system through additions or variations of the components. The comparison of Figs. 5b and 6 illustrates that even subtle chemical changes, such as replacing the counterion, may be important. In our most recent studies, we have made systematic changes that are more readily understandable in physical terms, such as variations in the sizes of the molecules [25], the charge density of the polyions [27], and the size and charge density of the surfactant aggregates [26].

Chain lengths

Figure 8 gives a compact overview of the phase behavior of binary mixtures of 10 different complex salts with water [25]. These complex salts are combinations of alkyltrimethylammonium surfactant ions

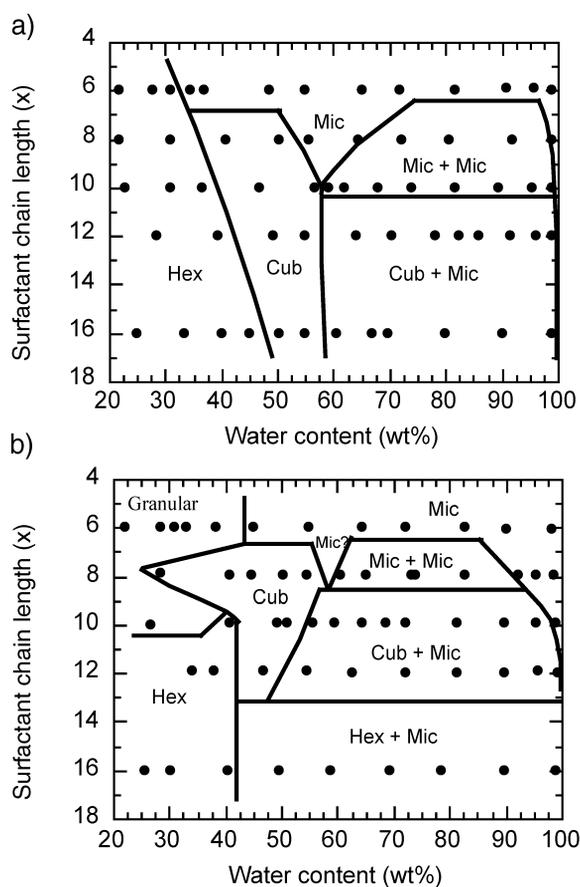


Fig. 8 A series of binary phase diagrams of mixtures of water with alkyltrimethylammonium PA complex salts of varying chain lengths, based on PA₃₀ (a) or PA₆₀₀₀ (b). From ref. [25].

of chain lengths ranging from C6 to C16, with PAs of two different weight average degrees of polymerization (30 or 6000). In the diagrams, the water content is given on the x -axis. Thus, the diagrams describe the outcome of dilution experiments, where water is progressively added to the various complex salts. Figure 8a shows the results for the short polyion. The sequence for the C16 complex salt at the bottom of the figure is already familiar from the C₁₆TAPA₃₀/water axes of the phase diagrams in Fig. 5: A hexagonal phase at low water content is replaced by a narrow cubic phase around 50 wt % water, after which additional added water ends up in a separate phase of essentially pure water. As the surfactant chain length is decreased, there is a gradual increase in the mutual solubility of the complex salts with water, and a disordered micellar phase eventually appears. Neglecting narrow two-phase regions, the sequence of phase regions changes, as the surfactant chain length is shortened, from hexagonal \rightarrow cubic \rightarrow cubic + water, over hexagonal \rightarrow cubic \rightarrow micellar \rightarrow concentrated micellar + dilute micellar, to hexagonal \rightarrow micellar. Interestingly, this variation in the phase sequence is exactly the same as that which occurs when NaPA₃₀ is added to a mixture of C₁₆TAPA₃₀ and water, see Fig. 5a. We believe that the underlying physics is the same in both cases. As the surfactant chains are made shorter, the fraction of non-micellized monomeric surfactant ions will increase. The aqueous complex salt can therefore be viewed as a solution of polyions neutralized by a mixture of monomeric and micellized counterions. The latter system is analogous to an aqueous mixture of a complex salt and excess polyelectrolyte.

Figure 8b again shows the effect of changing the surfactant chain length, but now in complex salts based on the long polyion. The same overall trends are seen as in Fig. 8a, but a new feature appears for the C16 salt, where the cubic phase has disappeared. At least two mechanisms could result in this effect. One is that the longer polyion decreases the curvature and induces a growth of the surfactant aggregate, just like the bromide ion in Fig. 6. The other explanation would be that the interaction with the longer polyion is sufficiently strong so as to pull the system into the more concentrated hexagonal region. As seen in Fig. 8, the stability range of the hexagonal phase of $C_{16}TAPA_{6000}$ with water (Fig. 8b) corresponds to a composition range where also mixtures of $C_{16}TAPA_{30}$ with water (Fig. 8a) are hexagonal.

Charge density of the polyion

The charge density of the polyion is expected to be an important variable. Our reference PA polyion offers two routes to introduce neutral comonomers. The simplest one is to mix the complex salt with the corresponding polyacid. In such a mixture, an equilibration will occur, so that the uncharged acrylic acid and the charged acrylate units freely mix among all polymer chains. The result is a solution of “copolymers” of acrylate and acrylic acid units. The other route is to synthesize a series of copolymers where acrylate units are copolymerized with selected neutral comonomers. In a very recent work, we have used both strategies [27]. Figure 9 shows the conventional triangular representation of the phase diagram for the ternary system $C_{16}TAPA_{6000}/PAA_{6000}/\text{water}$. On adding the polyacid progressively to the system, the cubic phase grows at the expense of the hexagonal phase, the wide miscibility gap decreases, and eventually the cubic phase disappears and is replaced by a disordered solution. Calculations of the micellar aggregation numbers from SAXS data show (Fig. 10) that the micellar size decreases as the molar fraction of charged units in the polyion decreases. We believe that the trends shown in Figs. 9 and 10, which were also confirmed by experiments using a series of random synthetic copolymers [27], can be understood in terms of the following physical picture. Neutral comonomers in the polyion chain will form loops that extend out in the aqueous domain. The configurational entropy of the loops gives rise to a loop–loop repulsion and, hence, a force in the direction of an increasing curvature. This will result in a change in aggregate geometry from rods to spheres and, eventually, a shrinking of the spheres.

It is interesting to compare the phase diagram in Fig. 9 with that in Fig. 5a above. In the latter phase diagram, ionic units with accompanying simple counterions, rather than neutral units as in Fig. 9, are introduced into a polymer where, originally, all repeating units are ionic units neutralized by surfactant ions. As would be anticipated, added ionic repeating units are much more effective than added nonionic units in closing the wide miscibility gap originating from the complex salt/water axis of the phase diagram.

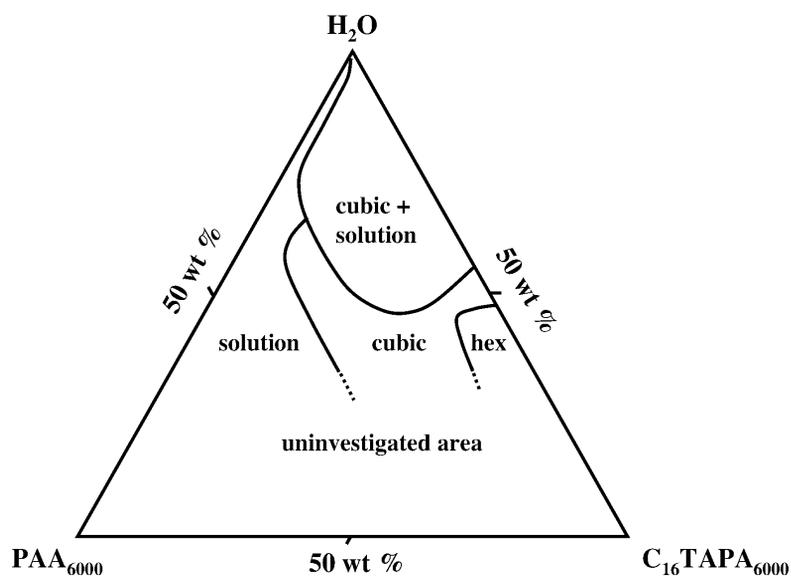


Fig. 9 Ternary phase diagram of the system PAA₆₀₀₀/C₁₆TAPA₆₀₀₀/water, showing the effect of introducing uncharged comonomers into the complex salt. From ref. [27].

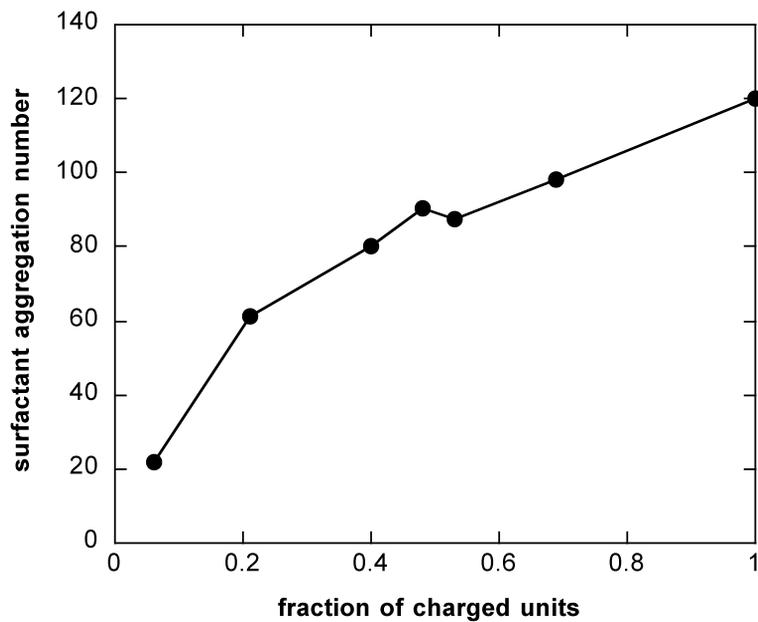


Fig. 10 Variation in the aggregation number of the C16 micelles with the fraction of charged repeating units in the polyion for the system shown in Fig. 9. Data from ref. [27].

Charge density of the surfactant aggregate

A standard procedure to decrease the charge density of a surfactant aggregate is to mix the surfactant with a “cosurfactant”. Typically, the cosurfactant is a long-chain alcohol that enters into the surfactant aggregates almost quantitatively, since it is practically water-insoluble. The hydroxide head group of the alcohol will be located at the aggregate surface, thus diluting the charges on the surface. Figure 11 shows the phase changes that result from adding decanol to aqueous $C_{16}TAPA_{30}$ [26]. As is known from similar studies of ternary mixtures based on conventional $C_{16}TA$ surfactants with bromide or sulfate counterions [32], added decanol very efficiently decreases the curvature of the surfactant aggregate. Thus, on progressive addition of decanol, the cubic phase disappears almost immediately in favor of a hexagonal phase which, in turn, is replaced by a wide lamellar phase. As expected, none of these phases swell very much in water; the polymeric counterions provide a very strong attraction between the large aggregates.

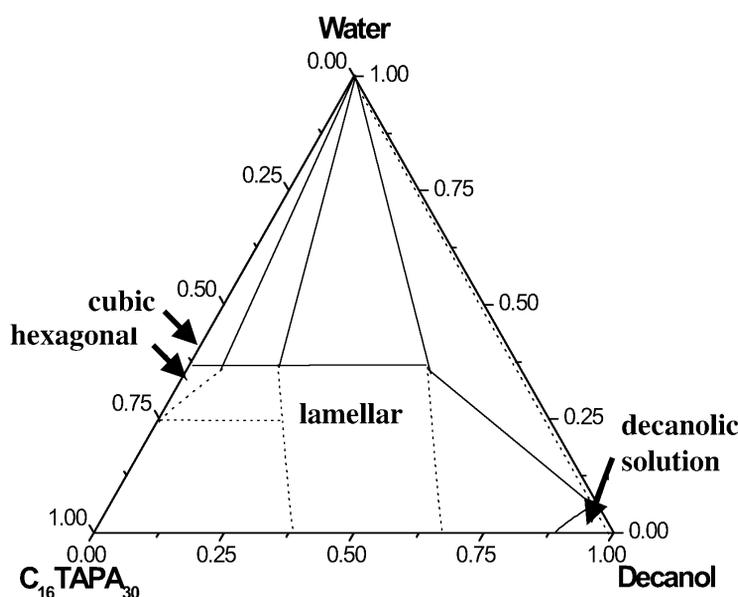
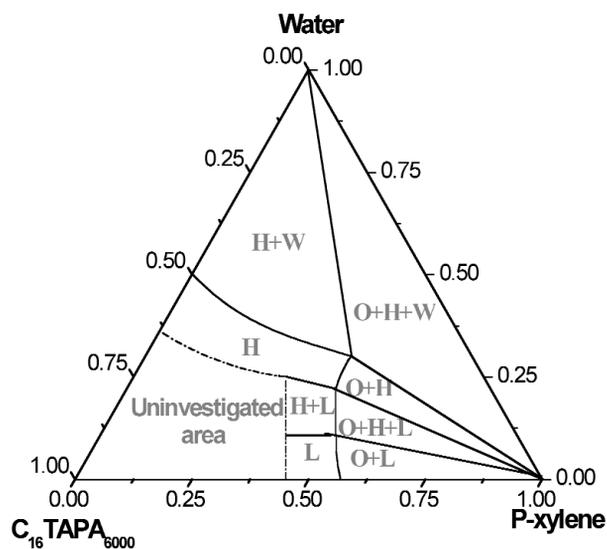


Fig. 11 Ternary phase diagram of the system $C_{16}TAPA_{30}$ /decanol/water, showing the effect of decreasing the charge density on the surface of the surfactant aggregate. From ref. [26].

Swelling the surfactant aggregate

If a nonpolar oil, rather than a polar alcohol, is added to a surfactant aggregate, the oil may dissolve in the interior of the aggregate and cause it to swell, rather than to change its geometry [26]. This is illustrated in Fig. 12. Here, the hexagonal phase of aqueous $C_{16}TAPA_{6000}$ can absorb a large fraction of *p*-xylene (Fig. 12a). As shown in Fig. 12b, the radius of the cylindrical aggregates in the hexagonal phase increases continuously by up to almost 70 % as the aggregates absorb *p*-xylene.

a



b

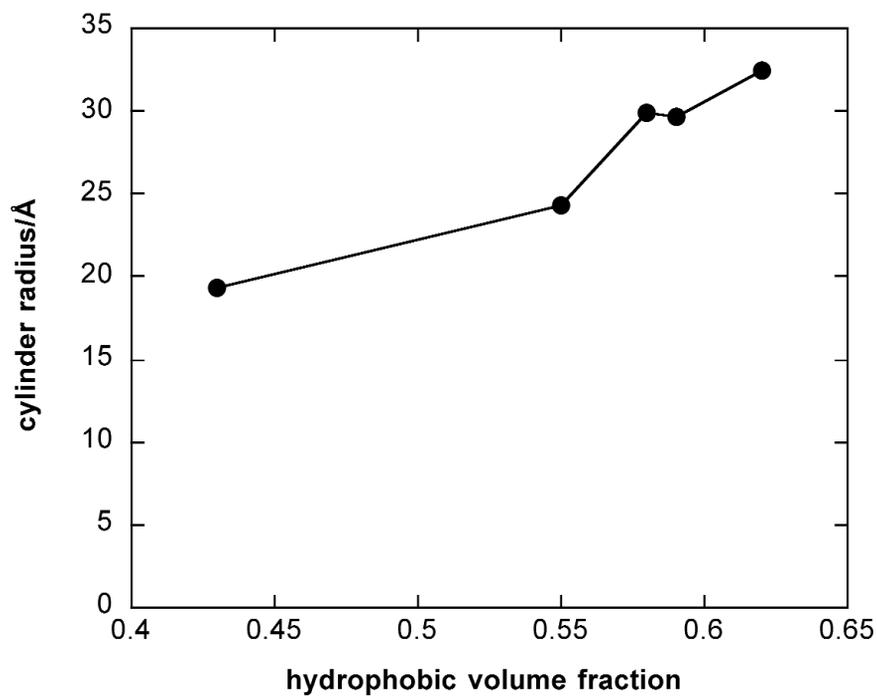


Fig. 12 Added nonpolar oil such as *p*-xylene is readily absorbed in the hexagonal structure of aqueous $C_{16}TAPA_{6000}$ (a) giving rise to an increase in the radius of the cylindrical surfactant aggregates (b). Data from ref. [26].

CONCLUSIONS AND OUTLOOK

The collective work summarized in this review represents a systematic attempt, using a minimum number of components, at an in-depth molecular understanding of the relations between molecular properties and the structures formed in aqueous mixtures of oppositely charged surfactants and polymers. Some of the simplest and most obvious polyion parameters have been varied, but many remain, such as stiffness, branching, and the presence of hydrophobic moieties. The phase diagrams resulting from our studies provide powerful predictions of, inter alia, the outcome of polymerization processes in surfactant system. These predictions are currently being tested in one of our laboratories.

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